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A Molecular Orbital Treatment of the Hexafluorovanadate(IV) and the Hexafluorovanadate(III) Ions

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The one-electron molecular orbital energy levels for VF_6^{2-} and VF_6^{3-} have been calculated using the Wolfsberg-Helmholz approximation. The agreement with experiment is very good for the d^1 ion, but less satisfactory for the d^2 ion VF_6^{3-}. Repulsion energies were estimated for VF_6^{3-} and corrections applied to the one-electron energy levels.

Introduction

The Wolfsberg–Helmholz[1] approximation for calculating one-electron molecular orbital energy levels has been carried out for the tetragonal vanadyl ion by Ballhausen and Gray,[2] and for the hexafluorotitanate(III) ion by workers in this laboratory.[3] In both cases the agreement with experimentally observed spectra was surprisingly good. Recently, one-electron molecular orbitals of the tetrahedral permanganate ion have been calculated[4,5] using corrections for ligand–ligand overlap and assuming no hybridization of ligand orbitals. In order to test further the applicability of the model used for the Wolfsberg–Helmholz calculations, the VF_6^{2-} and VF_6^{3-} ions are treated in the present work. Both ions are assumed to have O_h symmetry. The treatment of the VF_6^{2-} ion is essentially identical with that of the TiF_6^{3-} ion reported earlier. Since the systems are highly similar, the agreement with experiment should be equally good for VF_6^{2-} and TiF_6^{3-}. Such was observed to be the case.

In the case of the d^2 ion VF_6^{3-}, it is necessary to take into account the repulsion energies between the two electrons. The one-electron molecular orbital energy levels were calculated, and the spectrum was predicted by applying corrections in the form of the usual Coulomb and exchange integrals. The F_k values were estimated by two different methods: (1) calculation from the radial wave functions and (2) reduction of free ion values obtained from Moore's tables.[6] The agreement with the observed spectrum is fair, but not at all as good as was observed for the d^1 ions which have been treated.

Molecular Orbital Calculations for the VF_6^{2-} Ion

The VF_6^{2-} ion was assumed to consist of a regular octahedron of six F^- ions around one V^{4+} ion, with the V–F distance taken as the sum of the ionic radii.[7] The orbital transformation scheme in O_h symmetry is of course identical with that used for the TiF_6^{3-} ion.[3]

TABLE I

COULOMB ENERGIES FOR ATOMIC ORBITALS IN VF_6^{2-}, CORRESPONDING TO $V^{0.54+}$, $3d^{3.58}4s^{0.46}4p^{0.42}$

V		F	
Orbital	H_{11}, cm.$^{-1}$	Orbital	H_{22}, cm.$^{-1}$
3d	−108,220	2pπ	−127,200
4s	−88,220	2pσ	−136,900
4p	−52,680	2s	−272,220
		hyb. σ	−153,100

The solid lines in Figure 1 correspond (not to scale) to the one-electron molecular orbital energy levels obtained by solving the secular determinant

$$|H_{ij} - G_{ij}E| = 0$$

The group overlap integrals were obtained from atomic overlap integrals as described earlier.[3] The individual terms of the atomic overlaps were calculated on an IBM 7094,[8] using an interatomic distance of 1.95 Å. and the following atomic wave functions.

$$R(V_{3d}) = 0.476\phi_3(4.75) + 0.706\phi_3(1.70)$$

$$R(V_{4s}) = -0.02186\phi_1(22.395) + 0.07550\phi_2(8.475) - 0.1914\phi_3(3.85) + 1.0152\phi_4(1.25)$$

$$R(V_{4p})(d^3p) = 0.04559\phi_2(9.25) - 0.16996\phi_3(3.525) + 1.01317\phi_4(1.13)$$

$$R(F_{2s}) = -0.00411\phi_1(13.198) - 0.24286\phi_1(8.278) + 0.76464\phi_2(2.246) + 0.29770\phi_3(4.980)$$

$$R(F_{2p}) = 0.53155\phi_2(1.612) + 0.48890\phi_2(3.176) + 0.07255\phi_2(6.165)$$

where

$$\phi_n(\mu) = N_\mu r^{n-1}e^{-\mu r}$$

The fluorine wave functions were furnished by Prof. Roothaan,[9] and the vanadium functions are those for V^+ published by Richardson and co-workers.[10,11]

The values of the atomic overlap integrals obtained are: $S_{3d\sigma,2p\sigma} = 0.1361$, $S_{3d\sigma,2s\sigma} = 0.1630$, $S_{4s\sigma,2p\sigma} = 0.1082$, $S_{4s\sigma,2s\sigma} = 0.2379$, $S_{4p\sigma,2p\sigma} = 0.08456$, $S_{4p\sigma,2s\sigma} = 0.3690$, $S_{3d\pi,2p\pi} = 0.1012$, $S_{4p\pi,2p\pi} = 0.1456$. The degree of sp hybridization for the fluorine σ-orbitals was estimated as described earlier,[2,3] by minimizing the

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(1) M. Wolfsberg and L. Helmholz, *J. Chem. Phys.*, **20**, 837 (1952).

(2) C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **1**, 111 (1962).

(3) H. D. Bedon, S. M. Horner, and S. Y. Tyree, Jr., *ibid.*, **3**, 647 (1964).

(4) R. F. Fenske and C. C. Sweeney, *ibid.*, **3**, 1105 (1964).

(5) A. Viste and H. B. Gray, *ibid.*, **3**, 1113 (1964).

(6) C. E. Moore, "Atomic Energy Levels," U. S. National Bureau of Standards Circular 467, 1949 and 1952.

(7) S. Y. Tyree and K. Knox, "Textbook of Inorganic Chemistry," The Macmillan Company, New York, N. Y., 1961, p. 19.

(8) Located at the University of Chicago.

(9) C. C. J. Roothaan, University of Chicago, private communication.

(10) J. W. Richardson, W. C. Nieuwpoort, R. R. Powell, and W. F. Edgell, *J. Chem. Phys.*, **36**, 1057 (1962).

(11) J. W. Richardson, R. R. Powell, and W. C. Nieuwpoort, *ibid.*, **38**, 796 (1963).

TABLE II

GROUP OVERLAP INTEGRALS AND MOLECULAR ORBITAL ENERGIES FOR VF_6^{2-}

M.O. symmetry	G_{12}	G_{13}	Bonding levels $-E$, cm.$^{-1}$	c_1	c_2	c_3	Antibonding levels $-E$, cm.$^{-1}$	c_1^*	c_2^*	c_3^*
t_{2g}	0.2024		139,230	0.486	0.781		86,200	0.898	−0.658	
e_g	0.3189		167,160	0.392	0.803		65,450	0.979	−0.684	
a_{1g}	0.4722		165,840	0.326	0.804		11,330	1.087	−0.800	
t_{1u} (I)[a]	0.2929		153,670	0.0736	0.976	0.00814	19,910	1.089	−0.383	−0.425
t_{1u} (II)		0.2912	128,440	0.116	−0.0706	0.960				

[a] In the t_{1u} case, subscript 1 refers to V_{4p}, 2 to F_σ, and 3 to $F_{2p\pi}$. Calculated $10Dq$ = 20,750 cm.$^{-1}$.

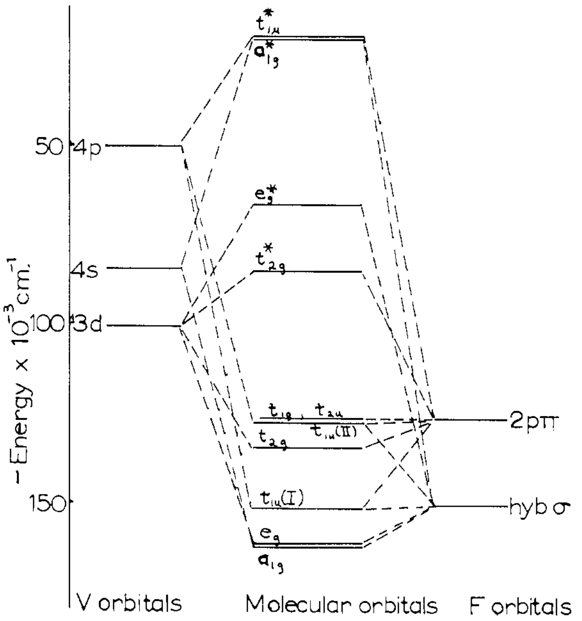

Figure 1.—One-electron molecular orbital energy level scheme for VF_6^{n-}. Ground state of ions: VF_6^{2-}, $^2T_{2g}(t_{2g}^*)^1$, VF_6^{3-}, $^3T_{1g}(t_{2g}^*)^2$.

TABLE III

OUTPUT POPULATION ANALYSIS FOR VF_6^{2-}, ASSUMED $3d^{3.58}4s^{0.46}4p^{0.42}$

Level	Electronic population owned by vanadium	
t_{2g}	1.880	total d = 3.584
t_{2g}^*	0.687	
e_g	1.017	
a_{1g}	0.460	total s = 0.460
t_{1u} (I)	0.160	total p = 0.421
t_{1u} (II)	0.261	

TABLE IV

COULOMB ENERGIES FOR ATOMIC ORBITALS IN VF_6^{3-}, CORRESPONDING TO $V^{0.51+}$, $3d^{3.74}4s^{0.41}4p^{0.34}$

V Orbital	H_{11}, cm.$^{-1}$	F Orbital	H_{22}, cm.$^{-1}$
3d	−101,000	2pπ	−127,200
4s	−84,700	2pσ	−136,900
4p	−49,920	2s	−272,200
		hyb. σ	−151,800

quantity VSIE/$S(\theta)$. The minimum occurred at 12% s and 88% p character. The atomic overlap integrals involving the fluorine σ-hybrid orbital were therefore: $S_{3d\sigma,\text{hyb}\sigma}$ = 0.1841, $S_{4s\sigma,\text{hyb}\sigma}$ = 0.1839, $S_{4p\sigma,\text{hyb}\sigma}$ = 0.2072.

The values of the group overlap integrals calculated from the atomic overlaps are listed in Table II.

The Coulomb energies (H_{ii} terms) were estimated as described previously.[3] The ultimate values obtained by the iteration process are listed in Table I and correspond to the assumed charge and electronic population indicated.

The off-diagonal terms were approximated in the manner used previously.[1-3]

$$H_{ij} = -2G_{ij}\sqrt{H_{ii}H_{jj}}$$

Solving the secular determinants gave the values of the molecular orbital energy levels listed in Table II and shown diagrammatically in Figure 1. The coefficients were calculated from the appropriate secular equations. Table III shows the population analysis for input and output charge and population.

Molecular Orbital Calculations for the VF_6^{3-} Ion

Calculation of One-Electron Molecular Orbital Energies.—The calculation of the one-electron molecular orbital energies for VF_6^{3-} was identical with the treatment used for the VF_6^{2-} ion. The only difference was in the sum of the ionic radii,[7] which gave an interatomic distance of 2.02 Å. The difference in distance gave different overlap integrals, which, in turn, required different Coulomb energies, charge, and population for a self-consistent result.

The atomic overlap integrals obtained are: $S_{3d\sigma,2p\sigma}$ = 0.1303, $S_{3d\sigma,2s\sigma}$ = 0.1473, $S_{4s\sigma,2p\sigma}$ = 0.1120, $S_{4s\sigma,2s\sigma}$ = 0.2275, $S_{4p\sigma,2p\sigma}$ = 0.09699, $S_{4p\sigma,2s\sigma}$ = 0.3592, $S_{3d\pi,2p\pi}$ = 0.08970, $S_{4p\pi,2p\pi}$ = 0.1374. The degree of sp hybridization obtained for the fluorine orbitals was 11% s and 89% p character. The overlap integrals for the hybrid orbitals are: $S_{3d\sigma,\text{hyb}\sigma}$ = 0.1718, $S_{4s\sigma,\text{hyb}\sigma}$ = 0.1811, $S_{4p\sigma,\text{hyb}\sigma}$ = 0.2106.

The Coulomb energies for the atomic orbitals are listed in Table IV, together with the charge and electronic population required for self-consistency of input and output values.

The molecular orbital energy levels calculated by solving the secular determinants are listed in Table V and shown drawn to scale in Figure 1. The population analysis is tabulated in Table VI.

Estimation of Repulsion Energies.—The value of $10Dq$ for the octahedral VF_6^{3-} complex may be taken as the difference between the e_g^* and t_{2g}^* energy levels. However, a comparison with the observed spectrum must take into account the change in repulsion energies involved in promoting one electron from the t_{2g}^* to the e_g^* level.

The repulsion energy between electrons in orbitals a and b may be written $E = J(\text{a,b}) - K(\text{a,b})$, where the

TABLE V

GROUP OVERLAP INTEGRALS AND MOLECULAR ORBITAL ENERGIES FOR VF_6^{3-}

M.O. symmetry	G_{12}	G_{13}	Bonding levels $-E$, cm.$^{-1}$	c_1	c_2	c_3	Antibonding levels $-E$, cm.$^{-1}$	c_1^*	c_2^*	c_3^*
t_{2g}	0.1794		135,110	0.406	0.844		85,600	0.932	−0.567	
e_g	0.2975		162,310	0.348	0.840		66,940	0.988	−0.626	
a_{1g}	0.4436		162,330	0.305	0.827		20,990	1.073	−0.749	
t_{1u} (I)[a]	0.2979		152,220	0.0626	0.979	0.00492	20,290	1.088	−0.379	−0.389
t_{1u} (II)[a]		0.2748	128,060	0.0969	−0.0560	0.969				

[a] In the t_{1u} case, subscript 1 refers to V_{4p}, 2 to F_σ, and 3 to F_π. Calculated $10Dq = 18{,}660$ cm.$^{-1}$.

TABLE VI

OUTPUT POPULATION ANALYSIS FOR VF_6^{3-}, ASSUMED $3d^{3.74}4s^{0.41}4p^{0.34}$

Level	Electronic population owned by vanadium	
t_{2g}	1.360	total d = 3.738
t_{2g}^*	1.547	
e_g	0.831	
a_{1g}	0.409	total s = 0.409
t_{1u} (I)	0.134	total p = 0.335
t_{1u} (II)	0.201	

Coulomb integral, $J(a,b)$, is defined as $(ab|e^2/r_{12}|ab)$, while the exchange integral, $K(a,b)$, is defined as $(ab|e^2/r_{12}|ba)$. The term e^2/r_{12} is the two-electron repulsion energy operator.

Therefore, for the change in repulsion energies involved in transferring one electron from the t_{2g}^* to the e_g^* level, we may write

$$E_{\text{excited}} - E_{\text{ground}} = E[(t_{2g}^*)^1(e_g^*)^1] - E[(t_{2g}^*)^2(e_g^*)^0] = J(t_{2g}^*,e_g^*) - K(t_{2g}^*,e_g^*) - J(t_{2g}^*,t_{2g}^*) + K(t_{2g}^*,t_{2g}^*)$$

Since the molecular orbitals involved are antibonding ones, and mostly centered on the vanadium atom, the Coulomb and exchange integrals may be approximated by using the integrals of the vanadium atomic orbitals, appropriately reducing the values to take complexing into account.

Rewriting the repulsion energy difference in terms of vanadium atomic orbitals, we obtain two possible functions

$$E_1 = J(xy, x^2 - y^2) - K(xy, x^2 - y^2) - J(xz, yz) + K(xz, yz) \quad (1)$$

$$E_2 = J(xy, z^2) - K(xy, z^2) - J(xz, yz) + K(xz, yz) \quad (2)$$

This particular choice of atomic orbitals is dictated by symmetry considerations. The configuration $(t_{2g})^2$ transforms like $^3T_{1g}$ under O_h symmetry. The configuration $(t_{2g}e_g)$ gives rise to a $^3T_{1g}$ state and a $^3T_{2g}$ state. Therefore, the transitions which ideally should be observed in the spectrum are $^3T_{1g}(t_{2g})^2 \rightarrow {}^3T_{2g}(t_{2g}e_g)$ and $^3T_{1g}(t_{2g})^2 \rightarrow {}^3T_{1g}(t_{2g}e_g)$. There will be a configuration interaction between the two T_{1g} states. Using the method of a descent in symmetry to D_{4h} symmetry as outlined by Ballhausen,[12] and applied by Bethe,[13] we find that $(xy, x^2 - y^2)$ and (xz, yz) both transform like $^3A_{2g}$ under D_{4h}. Since it is only the same symmetry species which can interact, we must use the configurations $(xz, yz) \rightarrow (xy, x^2 - y^2)$ as one of the $(t_{2g})^2 \rightarrow (t_{2g}e_g)$ transitions, corresponding to $^3T_{1g} \rightarrow {}^3T_{1g}$. Equation 2 corresponds to the promotion of a t_{2g} electron to the remaining e_g orbital, the d_{z^2}, and corresponds to the transition $^3T_{1g} \rightarrow {}^3T_{2g}$.

Writing the Coulomb and exchange integrals of eq. 1 and 2 in terms of Condon–Shortley parameters, as tabulated by Ballhausen,[14] we obtain

$$E_1 = 9F_2 - 45F_4 \quad (3)$$

$$E_2 = -3F_2 + 15F_4 \quad (4)$$

The V(III) free ion values for F_2 and F_4 may be obtained from data in Moore's tables.[6] These values are calculated to be $F_2 = 1310$ cm.$^{-1}$ and $F_4 = 90$ cm.$^{-1}$. There will be a reduction from the free ion values due to complexing by the fluoride ions. The fraction of this reduction, β, has been estimated by Clark[15] to be 0.75. Since an examination of Table V shows that only 77% of the two electrons in the t_{2g}^* orbital belong to vanadium, we shall reduce the free ion values of F_2 and F_4 by a factor of 0.77. Therefore, we estimate $F_2 = 1010$ cm.$^{-1}$ and F_4 and 70 cm.$^{-1}$ for VF_6^{3-}.

The foregoing assumptions give a value of 5980 cm.$^{-1}$ for E_1 and −1990 cm.$^{-1}$ for E_2. If these values for repulsion energy differences are added to $10Dq$ (the difference between the t_{2g}^* and e_g^* levels shown in Table IV), we obtain values of 16,670 and 24,640 cm.$^{-1}$. These corrections to the $t_{2g}^* \rightarrow e_g^*$ energy are shown as the distances between the dashed lines and the t_{2g}^* level in Figure 2.

A further correction to the one-electron molecular orbital levels must be applied. As mentioned above, there will be a configurational interaction between the $^3T_{1g}$ ground state and the $^3T_{1g}$ excited state, spreading the two levels farther apart than the simple additive correction shown above. The amount of this interaction is shown by the determinant[16]

$$\begin{vmatrix} F_0 - 5F_2 - 24F_4 - 8Dq - E & -6F_2 + 30F_4 \\ -6F_2 + 30F_4 & F_0 + 4F_2 - 69F_4 + 2Dq - E \end{vmatrix} = 0$$

Solving the determinant, we obtain a difference between the two roots of E of 25,840 cm.$^{-1}$. This means that there is an additional splitting of 1200 cm.$^{-1}$ between the two T_{1g} levels over and above the first cal-

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(12) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., New York, N. Y., 1962, p. 87.

(13) H. A. Bethe, *Ann. Physik*, [5] **3**, 133 (1929).

(14) Reference 12, p. 76.

(15) R. J. H. Clark, *J. Chem. Soc.*, 417 (1964).

(16) Reference 12, p. 83.

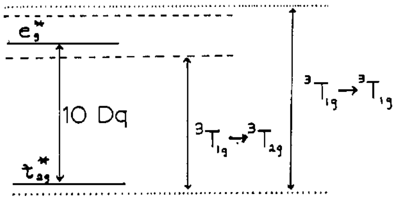

Figure 2.—Energy levels for VF_6^{3-} shown as corrections to $10Dq$ for one-electron molecular orbitals.

culated values. These levels are shown as dotted lines in Figure 2. Therefore, since the T_{1g} ground state is lowered 600 cm.$^{-1}$, the energies of the two possible transitions are $^3T_{1g}$ (ground) → $^3T_{2g}$ = 17,270 cm.$^{-1}$ and $^3T_{1g}$ (ground) → $^3T_{1g}$ = 25,840 cm.$^{-1}$.[16a]

Alternatively, the F_k values were computed[17] from the 3d radial functions for vanadium, as indicated by Ballhausen.[18] The F_2 and F_4 values were plotted as a function of charge on vanadium (Richardson[10] gives wave functions for all integral charges on vanadium). The values were read at $V^{0.51+}$, the charge calculated in our iteration process. This procedure gave the values $F_2 = 1120$ cm.$^{-1}$ and $F_4 = 75$ cm.$^{-1}$. The energies of the two predicted transitions then are calculated to be $^3T_{1g}$ (ground) → $^3T_{2g}$ = 17,190 cm.$^{-1}$ and $^3T_{1g}$ (ground) → $^3T_{1g}$ = 26,890 cm.$^{-1}$.

Results and Discussion

The calculated values for the d–d transitions in VF_6^{2-} and VF_6^{3-} are compared to the observed spectra in Table VII. The agreement in the VF_6^{2-} case is excellent, while the results are less satisfactory for VF_6^{3-}. The predicted transition for the d^1 ion is of course simply the difference between the t_{2g}^* and e_g^* levels. The poor results in the VF_6^{3-} case arise from a too-large value of $10Dq$ calculated from the one-electron energy levels. It should be noted that if $t_{2g}^* \rightarrow e_g^* = 16{,}100$ cm.$^{-1}$, the calculated values for the two transitions are 14,780 and 23,420 cm.$^{-1}$, still using $F_2 = 1010$ cm.$^{-1}$ and $F_4 = 70$ cm.$^{-1}$. These results suggest that the model used in the calculations is less than satisfactory for a d^2 ion. Since the levels calculated are one-electron molecular orbital energies, such discrepancy is not surprising. Almost surely the results would be improved by considering the effect on fluorine Coulomb energies in going from V(IV) to V(III). The Coulomb energies will be less for VF_6^{3-}, that is, the levels moved to a more positive value. Also, the effect should be greater on the pπ levels than on the hybrid σ, since the effect on the 2s level should be smaller, relatively, than on the 2p. Such changes would result in raising the t_{2g}^* level more than the e_g^* is raised, suitably reducing the value of $10Dq$.

It is possible that corrections for ligand–ligand overlap or adjustment of the factor F in the expression $H_{ij} = -FG_{ij}\sqrt{H_{ii}H_{jj}}$ would improve the results, as has been recently suggested.[4,5] Although neither of the former corrections has been tried, other changes in the model for VF_6^{2-} have been investigated, with unsatisfactory results. For example, a tetrahedral ion has been successfully treated using unhybridized s and p fluorine orbitals.[4,5] However, when we apply such a treatment to our octahedral molecules, the results are most unrealistic. Using the same starting energies for the ligand orbitals, and the same wave functions as described above, the value of $10Dq$ obtained for VF_6^{2-} is over 33,000 cm.$^{-1}$. In addition, the lowest bonding levels are naturally dropped below the −272,000 cm.$^{-1}$ assumed for the fluorine 2s level, and these lowest levels, when self-consistency is attained, have a negative population of vanadium electrons. For example, the lowest t_{1u} bonding level contains 6.13 fluorine electrons and −0.13 vanadium electron, according to a self-consistent calculation. Also, the highest antibonding levels, the a_{1g} and t_{1u}, have positive energy values.

TABLE VII

COMPARISON OF CALCULATED AND OBSERVED SPECTRA (CM.$^{-1}$)

Ion	Transition	Calculated	Observed
VF_6^{2-}	$^2T_{2g} \rightarrow {}^2E_g$	20,750	20,120[a]
VF_6^{3-}	$^3T_{1g} \rightarrow {}^3T_{2g}$	17,270[c]; 17,190[d]	14,800[b]
VF_6^{3-}	$^3T_{1g} \rightarrow {}^3T_{1g}$ (excited)	25,840[c]; 26,890[d]	23,250[b]

[a] Spectrum taken in this laboratory. [b] From values listed in ref. 15. The values 14,800 and 23,000 cm.$^{-1}$ were obtained earlier by C. J. Ballhausen and F. Winther, *Acta Chem. Scand.*, **13**, 1729 (1959). [c] Calculated for F_k values from Moore's tables. [d] Calculated for F_k values computed from wave functions.

Some improvement is shown when wave functions for F^- instead of F are used with the nonhybridized orbitals but $10Dq$ is still too high (about 22,000–23,000 cm.$^{-1}$); some antibonding levels have positive energies, and the lowest bonding levels still have a negative population of vanadium electrons.

The same calculations have been carried out using fluorine pure p orbitals only. The results (somewhat approximate) are shown in Tables VIII and IX. It is obvious that pure p orbitals give 10 Dq values far too small, even allowing for rather rough calculation.

TABLE VIII[a]

VF_6^{2-}, SELF-CONSISTENT CHARGE AND POPULATION: $V^{0.57+}$, $3d^{3.69}4s^{0.37}4p^{0.37}$

Symmetry	Input energy (cm.$^{-1}$) of V A.O.	Approx. energy (cm.$^{-1}$) of M.O. Bonding	Approx. energy (cm.$^{-1}$) of M.O. Antibonding
e_g	−108,500	−149,000	−82,000
t_{3g}	−108,500	−139,000	−86,000
a_{1g}	−90,900	−145,000	−66,000
t_{1u}	−54,000	−137,000	−128,700 −36,000

[a] $10Dq = 4000$ cm.$^{-1}$.

Considering the results obtained, it seems that the model using hybridized ligand orbitals gives the best agreement with experiment for the hexafluoro ions being considered here, although there are indeed shortcomings in the model. One serious objection is the fact that the nonbonding hybrid orbitals on the ligands

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(16a) NOTE ADDED IN PROOF.—It has been kindly pointed out by Dr. C. K. Jørgensen that the F_k values should be reduced by a factor of $(0.77)^2$. Using this value, the energies of the two transitions are calculated to be 17,525 and 24,040 cm.$^{-1}$, respectively.

(17) Using a Univac 1105 at the University of North Carolina.

(18) Reference 12, p. 21.

TABLE IX[a]

VF_6^{3-}, SELF-CONSISTENT CHARGE AND POPULATION: $V^{0.54+}$, $3d^{3.82}4s^{0.34}4p^{0.30}$

Symmetry	Input energy (cm.$^{-1}$) of V A.O.	Approx. energy (cm.$^{-1}$) of M.O. Bonding	Antibonding
e_g	−101,700	−146,000	−79,000
t_{2g}	−101,700	−135,000	−85,000
a_{1g}	−87,400	−144,000	−63,000
t_{1u}	−51,400	−137,000	−128,200 −35,000

[a] $10Dq = 6000$ cm.$^{-1}$.

have overlaps of the same order of magnitude as the bonding ones.[19] It has been pointed out that this model results in excessive covalency.[19] However, the value of 77% possession by vanadium of the t_{2g}^* electrons seems reasonable in view of the value of 0.75 which has been assumed for β in crystal field model calculations.[15]

The first charge-transfer band in both ions should correspond to the transition $t_{2u},t_{1g}(2p\pi) \rightarrow t_{2g}^*$. For VF_6^{2-}, this value is 41,000 cm.$^{-1}$ without correction for repulsion energies. The total estimated energy difference may be written

$$E(t_{2g}^* - 2p\pi) + 4J(2p\pi,t_{2g}^*) - 5J(2p\pi,2p\pi) + J(t_{2g}^*,t_{2g}^*) + 2K(2p\pi,2p\pi) - 2K(2p\pi,t_{2g}^*)$$

For VF_6^{3-}, the value is roughly the same (41,600 cm.$^{-1}$) before correction for repulsion energies. The total difference including corrections is

$$E(t_{2g}^* - t_{1g}) + 3J(t_{1g},t_{2g}^*) - 5J(t_{1g},t_{1g}) + 2J(t_{2g}^*,t_{2g}^*) + 2K(t_{1g},t_{1g}) - 2K(t_{1g},t_{2g}^*)$$

Since these corrections represent only a few thousand wave numbers, the first charge-transfer band should be observed quite far down in the ultraviolet region of the spectrum, probably at close to 50,000 cm.$^{-1}$.

It should be noted that the VF_6^{3-} and VF_6^{2-} repulsion energies differ only by $J(t_{2g}^*,t_{2g}^*) - J(t_{1g},t_{2g}^*)$. Since for the second term the orbitals are principally localized on different atoms, this difference may be estimated from the $3d^2$ repulsion energy as $4F_2 - 36F_4 = 4040 - 2520 = 1520$ cm.$^{-1}$, or the first VF_6^{3-} charge-transfer band should appear at approximately 2000 cm.$^{-1}$ higher energies than the corresponding VF_6^{2-} band. Such a prediction would also follow simply from a consideration of electronegativity differences in the vanadium ion in the two complexes.

The effective charge on the central metal was predictably similar for TiF_6^{3-}, VF_6^{2-}, and VF_6^{3-}. The slightly lower value obtained for VF_6^{3-} is also to be expected from considerations of nuclear charge and electron shielding.

The F_k values obtained from reduction of V^{3+} free ion values were within 10% of the values calculated for $V^{0.51+}$ from Richardson's 3d radial functions.[10] If one compares directly the values obtained for integral charges on vanadium, the results are not quite so similar, as shown in Table X.

Several attempts to obtain a good spectrum of K_2VF_6 in a KCl pellet failed, and the best resolution obtained showed the single d–d transition only as a shoulder on a charge-transfer band. In order to establish the position of the d–d band, a curve was drawn which matched the curvature of the charge-transfer band without the d–d shoulder. This background was then subtracted from the experimental curve, giving a nearly perfect bell-shaped curve with a maximum at 4970 Å. Determination of the spectrum at liquid nitrogen temperatures did not sharpen the band, and the position was essentially unchanged from that observed at room temperature. The experimental spectrum and the curve after subtraction of background are shown in Figure 3.

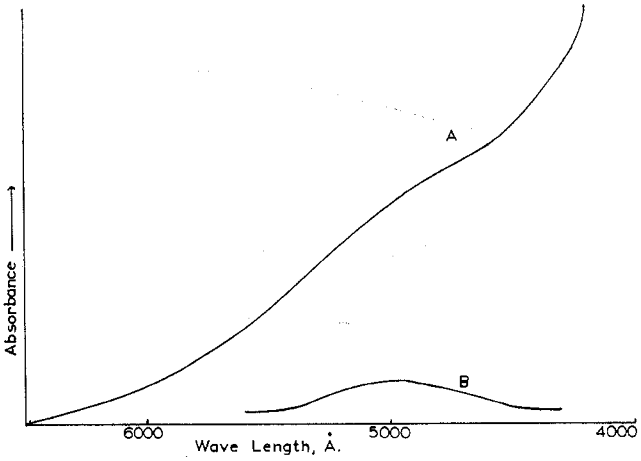

Figure 3.—Spectrum of K_2VF_6 in a KCl pellet: A, experimental curve; B, curve after subtraction of background.

TABLE X

COMPARISON OF COMPUTED F_k VALUES WITH VALUES OBTAINED FROM MOORE'S TABLES

Charge	F_2 (exptl.), cm.$^{-1}$	F_2 (computed), cm.$^{-1}$	F_4 (exptl.), cm.$^{-1}$	F_4 (computed), cm.$^{-1}$
+0.51	1010[a]	1120	70[a]	75
+1	900	1225	74	83
+2	1170	1425	83	98
+3	1310	1633	90	113

[a] $\beta = 0.77$.

Experimental

The K_2VF_6 used for experimental spectra was kindly furnished by Professor H. C. Clark.[20] Samples were ground with dry KCl in a nitrogen-filled drybox and loaded into a pellet die. The material was layered so that the pressed pellet was coated on either side with KCl. The spectrum was run on a Cary recording spectrophotometer.

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